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Mechano-chemical activation: an ecological safety process in the production of materials to stone conservation

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Abstract

The aim of this work is the assessment of the possibility to produce geopolymeric materials for the specific use in the field of consolidation of stone materials or as restoration mortars, through mechano-chemical activation of two solid precursors, quartz and kaolin. These starting materials were modified by grinding at different times and then the degree of reactivity of the obtained products was verified by studying the changes induced by the mechanical treatment on the crystalline structure and by determining the specific surface. Moreover the solubility and kind of alkaline solutions classically used for the production of geopolymeric materials (NaOH and KOH) was investigated together with other aqueous solutions at variable pH. The mechano-chemical activation process can achieve the result to reduce the use of alkaline solutions as activators of the starting raw materials in the production of consolidating solution for monument stone materials and to utilise natural materials in the production of restoration mortars compatible with the substrates to be restored.

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1. Introduction

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Mechanochemistry is defined as “a branch of chemistry dealing with the chemical and physico-chemical changes of substances in all states of aggregation due to the influence of mechanical energy. This is the first definition of mechanochemistry given in 1887 by Ostwald [1]. Mechano-chemical processing by high-energy milling is an innovative procedure, that improves the efficiency of mineral processing, via several factors such as those defined by Lin and Nadiv [2], Tkacova [3], Fernandez-Bertran [4] and Balaz [5]:

- generation of large new surfaces;
- formation of point defects;
- phase transformation in polymorphic materials;
- chemical reactions.

The benefits of the process, called also mechanical activation, include lower reaction temperatures, increased rate and amount of solubility, formation of water soluble compounds, namely increasing of reactivity of the treated materials. As a consequence, the processing can be performed in simpler and less expensive way during shorter times [5, 6].

There is a broad possibility of applications of mechanochemistry in mineral processing, extractive metallurgy, chemical engineering, building industry, coal industry, materials engineering, and waste treatment. The environmental aspects of these processes are particularly attractive [1, 7]. The main advantages in comparison with the traditional technological procedures are the following:

- decrease in the number of technological stages;
- excluding the operations that involve the use of solvents and gases.

Simplification of the processes and ecological safety characterise the mechano-chemical approach in technology. Taking into account what previously said, the application of this technique for the production of substances for the conservation of stone materials of historical and architectural interest is highly desirable for its environmental sustainability.

The aim of this work is the assessment of the possibility to produce geopolymeric materials for the specific use in the field of consolidation of stone materials or as restoration mortars, through mechano-chemical activation of the solid precursors selected by us (quartz and kaolin). Geopolymers are inorganic materials produced artificially in a process called "geopolymerisation" from aluminosilicates activated with alkaline oxides. Geopolymers can be produced with volcanic ash, tuff, pozzolane and artificial materials such as metakaolin, blast-furnace slag, etc.. These materials have proved to be particularly promising in various sectors (construction, ceramic, etc.). The mechano-chemical activation of the solid precursors, due to the high reactivity, can achieve two results:

- to reduce the use of alkaline solutions up to amounts not harmful to the monuments and the environment in the case of production of consolidating solutions;
- to have a natural material for the production of restoration mortars compatible with the substrates to be restored.

The possibility to realise reactive products has been verified by studying the changes induced by the mechanical treatment on the crystalline structure and by determining the specific surface. Moreover the solubility and kind of alkaline solutions classically used for the production of geopolymeric materials (NaOH and KOH) has been investigated together with other aqueous solutions at variable pH.

2. Experimental

2.1. Materials

As raw material, quartz and kaolin have been selected, the first because of the simple composition and

the second because widely used as a precursor of geopolymers. Quartz is of synthetic type, in granules from 0.2 to 0.8mm (Merck), the kaolin is natural, used in the ceramics industry (Poggi). The X-ray diffraction analysis showed that the latter is composed of kaolinite with impurities of 15% quartz.

2.2. Mechanical modifications

The starting materials were modified by grinding for 10', 40', and 320' in a planetary mill (Retsch Pulverisette 4) in steel jars with grinding ratio between the weight of the material to be ground and grinding media (steel balls of diameter 1 cm) of 1:50 and speed of the main disk of 1400rpm and of the planetary of 720rpm in friction.

2.3. Alkaline leaching

The leaching of the starting and activated materials was conducted by mixing 0.5g of solid with 20ml of solution for 17 hours under continuous stirring (KS 501 Digital, IKA Labortechnik) at vibration velocity of 110rpm. The variable considered is the kind of solution [H₂O, KOH, NaOH, NH₄OH]. All the solutions were obtained by diluting in distilled water Merck reagents. After shaking the solutions were immediately transferred into tubes for centrifugation in order to separate the solid from the liquid, adding to the solution 5ml of distilled water. Therefore the solutions with the powders were centrifuged (IEC CL31 Multispeed Centrifuge, Thermoscientific) for 15min at 4100rpm and the clear solution (20ml) was immediately drawn to and placed in sample holder for ICP OES analysis (PE 400).

2.4. Characterization of the starting and activated materials

The starting powders, mechanically activated, were analyzed by X-ray diffraction (XRD), differential thermoanalysis (TGA-DSC), solid state NMR (MAS-NMR), specific surface area (S_{BET}) and pore structure. The solutions extracted by alkaline leaching from the activated materials were analysed by induced coupled plasma spectrometry (ICP-OES).

2.4.1. X ray diffraction

XRD measurements were made with a Rigaku Rint 1200 instrument equipped with curved crystal graphite monochromator utilising Cu K α radiation. The evaluation of the reflection positions was carried out using a metallic silicon internal standard (50% of the weight of the sample). To determine the amount of amorphous material in the sample after grinding, the empirical relationship based on the ratio between the area of the background and the total area of diffraction peaks was utilised [8]. The method makes it possible to make a quick assessment of the amount of crystalline compound in the material

2.4.2. Thermal analysis

The TGA-DSC analyses (TA 600) were made to the following operating conditions: nitrogen atmosphere, 20 °C/min and alumina crucibles.

2.4.3. MAS-NMR

The MAS-NMR analysis were made with a Bruker (Biospin ASX 200 with CP-MAS) high resolution

spectrometer operating on ^1H at 200.13 MHz, equipped with high power decoupler for CP-MAS, multinuclear direct detection, magic angle facility and standard variable temperature unit.

2.4.4. Specific surface area and pore structure

At 77 K, nitrogen adsorption/desorption isotherms were measured using a Micromeritics ASAP 2020.

Prior to the measurement of absorption isotherms all samples were degassed at 300 °C overnight in order to remove adsorbed molecules from surfaces and from pores. Specific surface areas (S_{BET}) were calculated by applying the BET method to the linear section of the isotherms over 0.05–0.30 p/p^0 .

2.4.5. ICP-OES

The concentrations of silicon and aluminum in the solutions extracted from materials before and after the mechanical activation through alkaline attack, were measured using ICP-OES (PE 400). The solutions before the analysis were acidified with HNO_3 at 65%. 0.3 ml of nitric acid were added to the solution containing water, 1 ml to the solution of NH_4OH (1M), 1.3 ml to the 1M KOH solution and 1.4 ml to the 1M NaOH solution, 0.2 ml to the 0.1M KOH and NaOH solutions and 0.075ml to 0.01M KOH and NaOH solutions.

3. Results

3.1. X ray diffraction

The X-ray diffraction of ground kaolinite show a reduction of crystallinity of 70% with respect to the not ground just after 10' grinding, coming to have a total amorphization at 320' grinding. The decreasing of crystallinity for quartz is similar, but with different rate of decrease, and this difference is attributable to the different strength of the mineral (Fig. 1).

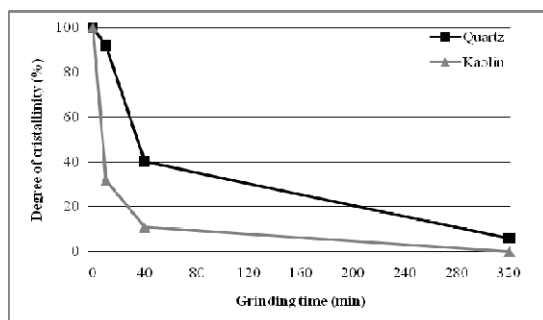


Fig. 1. Trend of quartz and kaolin crystallinity as a function of the grinding time

3.2. Thermal analysis

Thermogravimetric analysis of kaolin before grinding shows two important features, well known in literature [9]: the endothermic peak of dehydroxilation, located between 450 and 600°C, which denotes the transition from kaolinite to metakaolinite [9] and the exothermic peak of crystallization of the anhydrous aluminum silicate [mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)], located at about 1010°C (Fig. 2a). In samples of

ground kaolin, the endothermic peak resulting from the reaction of dehydroxilation tends to decrease in intensity and to shift towards lower values of temperature. The amount of energy needed for the dehydroxilation is reduced dramatically after only 40' of milling, reaching 33% of the initial value. After 320' grinding, the peak has almost disappeared. Similarly the loss of weight due to dehydroxilation, representing 12.3% of the sample, decreases to zero on the samples progressively more ground (Fig. 2b). Conversely, the crystallization of mullite occurs at the same temperature.

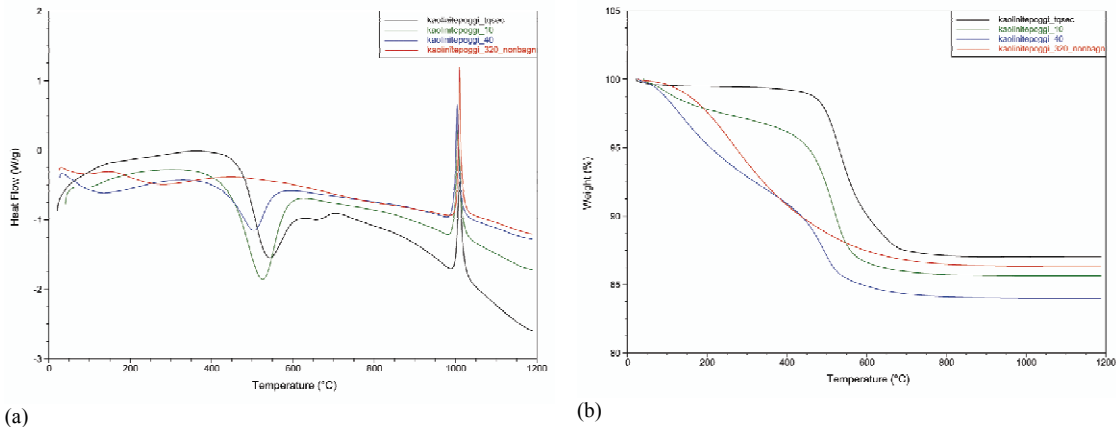


Fig. 2. Thermogravimetric analysis of kaolin: (a) the endothermic dehydroxilation peak ($\sim 500^{\circ}\text{C}$) and the exothermic crystallisation peak of mullite ($\sim 1010^{\circ}\text{C}$) are evidenced; (b) weigh loss curves for kaolin

Thermogravimetric analysis of not ground quartz, as already known [9], between 550 and 570°C shows only the endothermic peak of the transition form α to β form. The TGA-DTA measurements of the ground quartz show a gradual decrease of the endothermic peak, eventually disappearing entirely (Fig. 3). That represents an increase of structural disorder induced by milling and is usually reversible [9]. The ground quartz, just in the first minutes of treatment, is partly amorphous and as such can no longer turn its crystal structure into β . In the samples made at 320' milling amorphization is total (Fig.3).

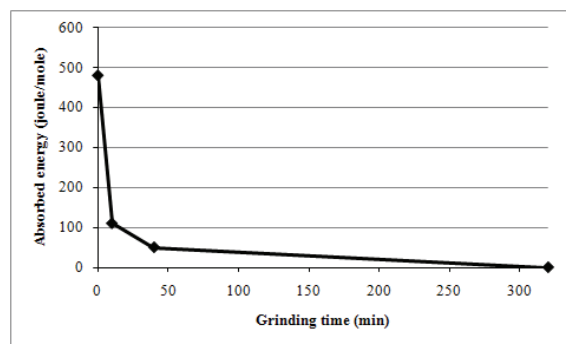


Fig. 3. Eenergy absorbed by quartz for the α - β transition (550 - 570°C), as a function of the grinding time

3.3. MAS-NMR

In the spectrum of silicon belonging to not ground kaolin (KTQ), only one peak centered at -91.3ppm is present, typical of a structure type SiQ^3 (1Al) (Fig. 4a). This structure is typical of the kaolin which has a layered structure consisting of a layer of octahedral aluminum hydroxide (gibbsite type) and a layer of tetrahedral silicon. Therefore in the notation used here the index "3" indicates a layered structure and 1Al means that the silicon atom has a single aluminum as second closest. In sample K40 (kaolin ground 40') a widening of the peak characteristic of a process of amorphization and the development of a peak at about -107ppm can be observed. This behaviour reveals the presence of a structure type SiQ^4 (0Al), ie a structure with a tetrahedral framework where the silicon has no aluminum as second closest (reported in literature as amorphous silica). In sample K320 (kaolin ground 320'), a further marked widening of the peaks can be observed which corresponds to a strong amorphization accompanied by an increase of the peak at about -107ppm, ie a structure type SiQ^4 (0Al).

The spectrum of aluminum of not ground kaolin shows a peak at 1.1ppm corresponding to aluminum with coordination 6, which is typical of octahedral aluminum hydroxide (gibbsite) (Fig. 4b). Sample K40, in addition to peak at 1.1ppm, shows two quite wide peaks at 28ppm and 55ppm, corresponding to aluminum with coordination 5 (28ppm) and coordination 4 (55ppm). Sample K320 shows a general broadening of the peaks and then a marked increase in amorphization and a clear peak at 28ppm and 55ppm, ie aluminum with coordination 5 and 4 respectively. The peak at 55ppm corresponds to structures type AlQ^4 (4Si). The milling process has a strong impact on the structure and on the short-range order both as regards silicon and aluminum.

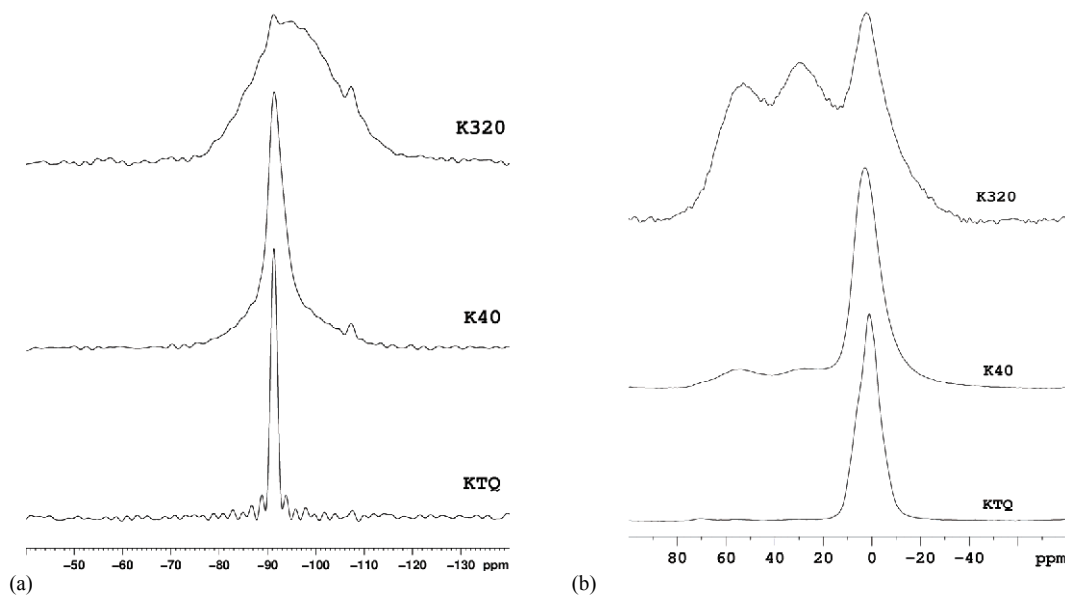


Fig. 4. MAS-NMR spectra for kaolin: (a) ^{29}Si and (b) ^{27}Al

The spectra of ^{29}Si for quartz, show that with increasing time of grinding not only an amorphisation of the material is produced, but also a structural change is clearly visible at 320' where the peaks belonging to new structures are clearly seen (Fig. 5).

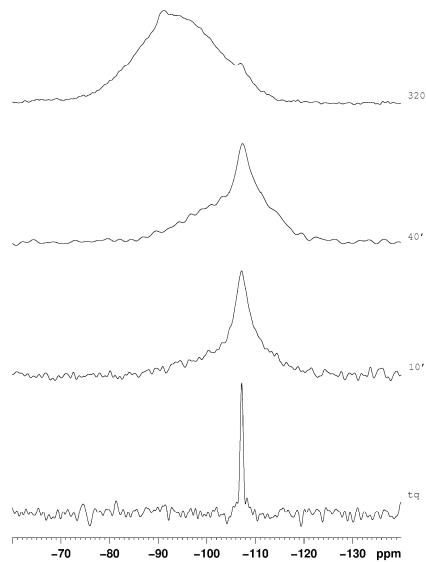


Fig. 5. MAS-NMR spectra for quartz: ^{29}Si

3.4. Specific surface area and pore structure

The BET specific surface area for not ground kaolin is $8.96 \text{ m}^2/\text{g}$. Results for kaolin samples are shown in Tab. 1. Tests run on a number of samples of ground kaolin show an increase in BET specific surface area for short grinding times (10') reaching values of $31.07 \text{ m}^2/\text{g}$. Once a certain grinding time has been reached, BET specific surface area values become constant. These data are in agreement with those of literature [10]. All isotherms are of type II in the BDDT classification. The nitrogen adsorption/desorption isotherms are shown in Fig. 6a The shape of the isotherms indicate the presence of slit-shaped pores typical of clay minerals.

Table 1. BET values of the superficial area as a function of the milling time

Grinding time (min)	BET Surface area (m^2/g)	
	Kaolin	Quartz
0	8.96	0.06*
10	31.07	8.33
40	17.85	17.97
320	22.52	22.93

*literature datum [the dimensions of not ground quartz ($200\mu\text{m}$ - 0.8mm) fall outside the range that can be investigated with this technique]

The BET specific surface area for not ground quartz is $0.06 \text{ m}^2/\text{g}$ [data from 11]. Results for quartz samples are shown in Tab.1. Ground quartz samples show an increase in BET specific surface area after mechanical treatment reaching values of $22.93 \text{ m}^2/\text{g}$ after 320' of milling. The nitrogen adsorption/desorption isotherms are shown in Fig. 6b.

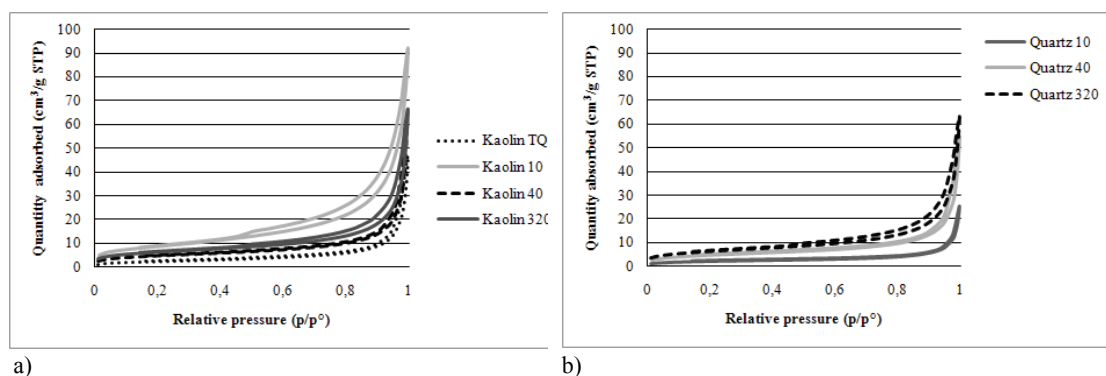


Fig. 6. Absorption/desorption isotherms for kaolin (a) and for quartz (b). As regards not ground quartz, the dimensional range of particles is not investigable with this technique

3.5. Alkaline leaching

The extraction tests with various solutions for kaolin not ground and mechanically activated show an increase of extraction of aluminum and silicon with increasing grinding time, although in a non-linear trend (Tabs. 2-3). This is probably due to the low hardness of this material that already after 10' grinding is completely amorphous (Fig.1). Then structural rearrangements are produced that lead to a decrease in specific surface area (Tab. 1) at 40' grinding followed by a further increase. Evidently 40' corresponds to a time "critical" for the mechanical action on the kaolin, which is reflected on the extractability of silicon and aluminum. The NMR data indicate changes in the coordination of aluminum from VI to IV and V, corresponding to 40' grinding for silicon and indicate the occurrence of a tetrahedral type structure which is accompanied by the amorphization of the material. Only data that disagree are those for 0.1M solutions of KOH and NaOH and 1M of KOH that in correspondance to this grinding time show an increase in extractability of aluminum followed by a decrease.

Table 2. Concentration of silicon (ppm) extracted from kaolin as a function of the grinding time

Grinding time (min)	H ₂ O	NH ₄ OH (1M)	NaOH (1M)	NaOH (0.1M)	NaOH (0.01M)	KOH (1M)	KOH (0.1M)	KOH (0.01M)
0	0.7	3.3	14.4	12.5	5.0	10.3	7.6	2.7
10	3.5	5.3	622.0	109.7	18.3	344.0	49.3	42.1
40	2.9	3.6	437.0	85.7	8.9	263.0	39.6	11.3
320	2.3	6.2	640.0	120.6	23.3	338.0	69.5	42.3

Also in this case, the highest extraction is obtained with the more concentrated solutions of NaOH and KOH for 320' grinding (values around 600ppm for silicon and 800ppm for aluminum). These amounts are considerably higher than those reported by some authors and with considerably more concentrated solutions [12]. In the case of kaolin, the extraction of silicon and aluminum in water is not affected by the mechanical action while in case of extraction with ammonium hydroxide there seems to be a small increase in the concentration of aluminum in solution. Some authors have found that in kaolin the cation exchange capacity increases with increasing grinding time [10]. This fact is based on the theory that the exchange positions are located on the crystal edges and an increase in the exchange capacity is due to the

increase in the number of edges [13]. One might think that these new sites are able to capture ammonium in such a way to determine a mildly leaching action towards aluminum. Still in the case of kaolin, it is possible to see that in the material mechanically activated aluminum is generally extracted in quantities greater than silicon. Also this fact was explained by different authors with a structural change [14, 15] with higher reactivity at the lowest Al VI content in the material. The mechanical treatment of kaolinites alters the octahedral Al layer to a greater extent than the tetrahedral layer enriching the surface of kaolinite particles with Al. The structural deterioration caused by the mechanical treatment alters the coordination number of Al and shifts it to outer sites, which facilitates its extraction. The MAS-NMR and TGA-DSC data confirms that the mechanical complete disintegration of the original kaolinite structure means the formation of an unstable metakaolinite form and the change of the Al atom coordination number from 6 to 4, or to 5. Both forms with the coordination numbers 5 and 4 are reactive, which means ready for hydration. The dehydroxylation is accompanied by kaolinite amorphization, which is favorable to a surface dissolution of clay particles in an alkaline solution.

Table 3. Concentration of aluminium (ppm) extracted from kaolin as a function of the grinding time

Grinding time (min)	H ₂ O	NH ₄ OH (1M)	NaOH (1M)	NaOH (0.1M)	NaOH (0.01M)	KOH (1M)	KOH (0.1M)	KOH (0.01M)
0	1.0	1.4	6.4	5.1	2.9	8.0	5.4	2.7
10	8.9	28.0	673.0	163.5	80.8	419.0	129.2	42.1
40	1.8	42.3	648.0	195.2	25.5	518.0	165.5	11.3
320	2.4	25.0	816.0	157.3	47.3	459.0	110.0	42.3

As regards quartz, the extraction tests with solutions at different pH indicate in general an increase in the extraction of silicon with increasing grinding time (Tab. 4), in agreement with a decrease in the crystallinity of the material (amorphization) and an increase in specific surface (Fig. 1 and Tab. 1). The solutions that show a higher capability of extraction are NaOH and KOH, with higher values for higher alkalinity (about 4000ppm) at 320'. Even for lower alkalinity, the solutions of NaOH and KOH show non-negligible values of concentration of extracted silicon (about 200ppm). The concentrations obtained are extremely high and correspond to about 40-45% of dissolved solid (as SiO₂) which can be referred to the dissolution of the amorphous layer. This layer would develop more and more around the quartz particles starting from a few nanometers and increasing up to several tens of nm and finally after prolonged grinding, the entire particles would become amorphous [16]. The increase in the amorphisation of quartz is shown both by NMR and XRD data. Water shows a slight increase in silicon extraction always compatible with the decrease of crystallinity of the material passing from values around 1ppm, for not treated quartz up to a maximum of about 15ppm for 320' ground quartz (Tab. 4). These values, obtained in tests with distilled water, are in agreement with the concentration of silicon in natural waters, where the concentration in presence of quartz is between 2-5ppm and in presence of amorphous silica is between 36-70ppm [17]. Even in the case of ammonium hydroxide, the values of extracted silicon are quite high, around 250ppm for 320' grinding (Tab. 4).

Also these values appear to be in agreement with those of literature [18] but obtained for reaction times 20 times (300-500 hours) higher than those used in our work. Moreover in case of attack with ammonium hydroxide, after about 10 minutes of grinding the maximum values of silicon extracted are reached, the following datum remaining practically unchanged around 250ppm.

Table 4. Concentration of silicon (ppm) extracted from quartz as a function of the grinding time

Grinding time (min)	H ₂ O	NH ₄ OH (1M)	NaOH (1M)	NaOH (0.1M)	NaOH (0.01M)	KOH (1M)	KOH (0.1M)	KOH (0.01M)
0	0.6	2.4	12.2	6.5	1.1	21.4	1.9	7.6
10	3.8	298.0	558.0	143.4	41.8	706.0	95.8	19.0
40	11.3	235.0	1692.0	1060.0	281.3	1870.0	1440.0	206.5
320	16.1	221.0	4000.0	2520.0	254.1	4290.0	1900.0	201.9

4. Conclusions

The work confirms that structural modifications due to the mechanical activation of the solid precursors (kaolin and quartz) promote an increase of extraction of aluminum and silicon with increasing grinding time allowing to utilize less dangerous solutions in the preparation of geopolimeric products for the conservation of stone materials. In particular regarding the behavior of the mechanical activated kaolin, the following aspect can be observed:

- the extraction of Si and Al has a not linear trend: two peaks are identified at 40' and 320';
 - the highest extractions of Si and Al are obtained with the more concentrated solutions of NaOH and KOH at 320' (Si~600ppm and Al~800ppm);
 - good extraction of Si and Al are obtained also with less concentrated solutions of NaOH/ KOH at 320';
 - negligible amounts of Si and Al are extracted with water and NH₄OH;
- As regard the behavior of the mechanical activated quartz, it can be noticed that:
- the extraction of Si increases linearly with increasing grinding time;
 - the highest extraction of Si is obtained with the more concentrated solutions of NaOH and KOH at 320' (~ 4000ppm);
 - good extractions of Si are obtained also with less concentrated solutions of NaOH, KOH and NH₄OH (~200ppm) at 320';
 - negligible concentration of Si is extracted with water.

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